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<p>Chromatographic effects from transition metal ion association with the silica used as packing materials in high-performance liquid chromatography were emphasized with special attention given to their catalytic properties and methods for studying them. Retention changes for selected solutes resulting from silica modification were also studied. For rate process analysis, a statistical method based on the first moment of the overall elution profile was developed for first-order type chemical reactions under special conditions. This approach alleviated difficulties in resolving and analyzing reactant and product overlap, and it also facilitated the study of features associated with catalysis such as adsorption. With this approach as a start and hydroquinone oxidation as a probe reaction, significant progress was made toward developing a stable, reproducible, iron(III) ion-modified silica stationary phase with considerable catalytic activity. Studies</p> <p style="text-align: right;">(over)</p>			
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of preparations in both non-aqueous and aqueous media showed the latter to be advantageous for preparing active modified silicas. Iron(III) modified silica exhibited retention properties which were superior to those of silica for some chromatographic separations. Silica modified with chromium(III) ions also showed catalytic activity. Further investigation led to the discovery that ferric ion-modified silica was a superior catalyst for on-column triphenyl phosphite oxidation to triphenyl phosphate under relatively mild conditions ($<50^{\circ}\text{C}$). In the course of this work, two comprehensive reviews explaining the analysis and use of modern liquid chromatographic columns and packings in a variety of ~~recovery~~ applications were completed and published. Possibilities for more extensive applications were discussed including the removal of environmentally undesirable materials.

REACTOR STUDIES OF METAL IONS ASSOCIATED
WITH CHROMATOGRAPHIC SILICA

FINAL REPORT

STANLEY H. LANGER

APRIL 15, 1993

U.S. ARMY RESEARCH OFFICE

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Reactor Studies of Metal Ions Associated with Chromatographic Silica

This investigation established that catalytic liquid phase chromatographic reactors could be improved to a significant extent and were feasible for carrying out chemical transformations. A number of new possibilities emerged. The effort continued to emphasize iron although other ions were also investigated. Fe(III) ions associated with silica are not only very stable, catalytically active, and ubiquitous but their immobilization and means for studying their catalytic properties serve as a model for comparing immobilization effects with other ions. Among other ions investigated preliminarily were those from chromium, nickel and cobalt which can originate from stainless steel alloys utilized in chromatographic equipment. As part of this effort, two reviews were assembled. One of these, for a book on Production Scale Chromatography was on "gas and liquid chromatographic reactors." A unique feature was incorporation of a discussion based on our collaborative work on the use of liquid crystals as stationary phase reaction media for gas chromatography and their advantages. The other broad-based review for the Journal of Chromatography addressed "reaction kinetics and kinetic processes in modern liquid chromatography." Multifold applications of liquid chromatographic reactors with a wide range of materials were described and illustrated. This included many biotech type phenomena as well as significant basic chemistry.

In addition to extensive ion immobilization experimental work involving both aqueous and non-aqueous media four other areas received special attention. These included the following: (1) An overall rate analysis of kinetic processes in the liquid chromatographic reactor. Beyond chemical kinetics, consideration of mass transfer, adsorption and desorption processes were also covered. (2) Characterization of ion-modified silicas using retentions of probe type compounds such as phenols, amines, and esters. In addition to basic concern with the properties of immobilized ions this was because ion modified silicas can also be of particular interest to chromatographic investigators who want to accomplish special separations. (3) Catalytic activity, its location in the column and its nature. This was accomplished using various reactive species as well as reducing and oxidizing agents and subsequent testing. (4) Phosphite oxidations and related reactions. This was a consequence of our discovery that iron immobilized on silica is a particularly effective catalyst for triphenyl phosphite oxidations to phosphate in the liquid chromatographic reactor under mild conditions. Others, in the patent literature, have indicated a need for much higher temperatures ($>100^{\circ}\text{C}$) and oxygen under high pressures to carry out this reaction.

Many details of the work above are described in the list of publications included in this report. A number of phenomena described in these papers indicate that this area is a very promising one for further investigation.

PUBLICATIONS

1. "Rate Process Analysis in the Liquid Chromatographic Reactor: An Application of the First Statistical Moment", C. Y. Jeng and S. H. Langer, Industrial and Engineering Chemistry, 30, 1489 (1991).
2. "Hydroquinone Oxidation Kinetics in Adsorptive Liquid Chromatographic Beds", C. Y. Jeng and S. H. Langer, J. of Chromatography, 556, 383 (1991).
3. "Reaction Kinetics and Kinetic Processes in Modern Liquid Chromatographic Reactors", C. Y. Jeng and S. H. Langer, J. of Chromatography, 589, 1-30, (1992). (A Review)
4. "Gas and Liquid Chromatographic Reactors", J. Coca, G. Adrio, C. Y. Jeng and S. H. Langer, in "Preparation and Production Scale Chromatographic Methods and Application", ed. G. Ganetsos and P. E. Barker, Marcel Dekker, N.Y. (1993), pp. 449-475.
5. "Iron (III) Ion-Modified Chromatographic Silica Preparations and Characterization", Z. Deng, J. Z. Zhang, A. B. Ellis and S. H. Langer, J. of Chromatography, 626, 159 (1992).
6. "Catalytic Oxidation of Triphenyl Phosphite with Ferric Ion-Modified Chromatographic Silica", by Z. Deng, J. Z. Zhang, A. B. Ellis and S. H. Langer, J. of Liquid Chromatography, 16(5), 1083 (1993).

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